On the structure of the first hydration layer on NaCl(100): Role of hydrogen bonding

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The authors have investigated the structure and energetics of the first hydration layer on NaCl(100) by means of density functional calculations. They have analyzed in detail the role of the hydrogen bond between the adsorbed molecules for the determination of the most favorable structures. They have shown that, using the water dimers as basic building blocks, very stable structures can be constructed. They discuss here two important examples: (i) a model with (1×1) periodicity at 2 ML coverage, and (ii) icelike bilayers with a $c(4\times2)$ unit cell at 1.5 ML. Both structures present high adsorption energies per water molecule of ~570 meV, in comparison to the 350 meV adsorption energy obtained for the previously studied (1×1) structures composed of weakly interacting monomers. Based on these findings, they propose an interpretation for the experimental observations of Toennies *et al.* [J. Chem. Phys. **120**, 11347 (2004)], who found a transition of the periodicity of the first hydration layer on NaCl(100) from (1×1) to $c(4\times2)$ upon electron irradiation. According to the model, the transition would be driven by the partial desorption of (1×1) bilayer structures corresponding to a local coverage of 2 ML and the further rearrangement of the remaining water molecules to form a quasihexagonal structure with $c(4\times2)$ periodicity at coverage close to 1.5 ML. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2743411]

I. INTRODUCTION

Chemical reactions on NaCl surfaces have been widely investigated[1,2] since NaCl is one of the most important components of tropospheric aerosols, especially in oceanic regions.[3] Many studies have demonstrated the catalytic role of water adsorbed on these aerosols for reactions with gaseous pollutants, such as HNO_3, N_2O_5, and NO_2,[1,4] and also with tropospheric ozone.[5] In spite of this extensive research, the structure of the initial adsorption layers of water on NaCl is still a subject of debate.

The adsorption configuration clearly depends on the competition between the water-surface interaction and the hydrogen bonding between the water molecules. Close to the monolayer regime these interactions appear to be almost balanced and, as a consequence, the symmetry and structure of the adsorbed layers have not been clearly established. On one hand, investigations based using low energy electron diffraction (LEED) reported a scattering pattern consistent with a $c(4\times2)$ periodicity of the adsorbed layer.[6,7] On the other hand, helium atom scattering (HAS) experiments indicated a (1×1) periodicity.[8] From the theoretical side, several structures exhibiting (1×1) and $c(4\times2)$ periodicities have been suggested.[9–13] Table I presents the theoretical adsorption energies per water molecule of previously proposed geometries of the water layer at coverages of 1 and 1.5 ML obtained with a variety of computational techniques. The values obtained in the present work are also shown in Table I. The adsorption energies are decomposed in the contributions from water-surface interaction and water-water hydrogen bonding, when such separation is available.

So far, most of the adsorption configurations with (1×1) periodicity have been proposed for 1 ML coverage, understood as one water molecule per Na site. In these structures, the molecules are too far from each other for the formation of strong hydrogen bonds between them. Thus, their orientation on the substrate and their adsorption energy are mainly determined by the water-surface interactions (see the values presented in Table I). Regarding the structures with $c(4\times2)$ periodicity, most of them have been suggested for a coverage of 1.5 ML. They present more compact water layers following a pattern that resembles the characteristic bilayers of crystalline ice. Such a perfect hexagonal structure

TABLE I. Theoretical adsorption energies, E_{ads} (eV), for different geometries of the adsorbed water layer at 1, 1.5, and 2 ML coverages (θ). The third and fourth columns correspond to the energy contribution from the water-surface interaction, $E_{w\text{-surf}}$ (eV) and the water-water hydrogen bonding, $E_{H\_bonding}$ (eV). The last four rows (in bold) correspond to our results.

	θ (ML)	E_{ads} (eV)	$E_{w\text{-surf}}$ (eV)	$E_{H\_bonding}$ (eV)
1×1 monolayer[a]	1	0.318	0.226	0.092
$c(4\times2)$ bilayer[a]	1.5	0.457	0.183	0.274
1×1 monolayer[b]	1	0.630	0.570	0.060
$c(4\times2)$ bilayer[b]	1.5	0.700	0.150	0.550
1×1 monolayer[c]	1	0.468	0.321	0.147
2×2 monolayer[d]	1	0.537	⋯	⋯
$c(4\times2)$ bilayer[d]	1.5	0.567	⋯	⋯
1×1 monolayer[e]	1	0.316	⋯	⋯
1×1 monolayer	**1**	**0.350**	**0.297**	**0.053**
1×1 bilayer	**2**	**0.571**	**0.181**	**0.390**
$c(4\times2)$ bilayer *A*	**1.5**	**0.572**	**0.186**	**0.386**
$c(4\times2)$ bilayer *B*	**1.5**	**0.522**	**0.111**	**0.411**

[a]Park *et al.*, DFT-GGA results (Ref. 9).
[b]Meyer *et al.*, DFT-LDA results (Ref. 13).
[c]Taylor *et al.*, periodic Hartree-Fock results (Ref. 11).
[d]Engkvist and Stone, results using model potentials derived from the intermolecular perturbation theory (Ref. 12).
[e]Jug and Geudtner, quantum chemical results using a semiempirical method (SINDO1) (Ref. 10).

can be assumed to be the preferred one when the water-water interaction clearly dominates over the water-surface interaction. However, the bonding with substrate forces the water layer to adopt a compromise between the hexagonal structure preferred by the water molecules and a structure more in registry with the surface. Consistent with this compromise, several "quasihexagonal" arrangements have been suggested in previous work for a coverage of 1.5 ML.[9–13] Hereafter, we will call these configurations quasihexagonal because they do not completely follow the ideal hexagonal structure of the water bilayer in ice, but in most cases they present two broken hydrogen bonds in each of the "hexagons" that form the perfect bilayer. In spite of the presence of these defects, the hydrogen bonding has a predominant contribution to the adsorption energy compared with the contribution from the water-surface interaction. This is reflected in Table I. The much shorter hydrogen bonds of the $c(4\times2)$ structures at 1.5 ML lead, using the same theoretical method, to adsorption energies significantly higher than those for the (1×1) structures at 1 ML.

The debate about the (1×1) vs $c(4\times2)$ periodicity for the first hydration layer on NaCl(100) has been experimentally studied by Toennies *et al.*[7] These authors made a sequence of experimental observations using HAS and LEED under ambient conditions. Initially, their HAS experiments found diffraction peaks consistent with an ordered (1×1) surface layer, while subsequent LEED measurements on the same sample indicated a $c(4\times2)$ structure. Finally, they carried out HAS measurements, after the LEED current was applied, reporting a stable $c(4\times2)$ overlayer. The change in the overlayer periodicity was attributed to the electron irradiation during the LEED experiment, leading to a reorientation of water molecules and a compression of the layer, since (1×1) periodicity was supposed to occur at 1 ML coverage whereas the $c(4\times2)$ structure was tentatively assigned to 1.5 ML coverage. However, the most frequent experimental observation is that electron irradiation induces desorption of adsorbates, such as water molecules, from various surfaces.[14,15] Therefore, one should expect a reduction of the water coverage by appliance of LEED, in contrast with the interpretation of "compression" given by Toennies *et al.*

In the present work we propose a different scenario to understand the observations of Toennies *et al.* We first study the relaxed configuration of a water dimer on NaCl(100) at low coverage. In agreement with previous works,[9,12] the adsorption energy per molecule for an adsorbed water dimer is much higher than the typical values obtained for (1×1) structures at 1 ML. Therefore, using the water dimers as the building blocks one should be able to construct very stable configurations for the first hydration layer. Indeed, we have constructed a very stable (1×1) structure at the larger coverage of 2 ML by packing water dimers. We also study here two quasihexagonal $c(4\times2)$ models at 1.5 ML. These $c(4\times2)$ structures are comparable to previous proposals in the literature,[9,12,13] although in the present case, the smaller amount of broken hydrogen bonds leads to higher adsorption energies. The obtained adsorption energies per water molecule are very similar in these (1×1) and $c(4\times2)$ configurations. We propose that the high stability of our (1×1) model provides a likely scenario to explain the controversy on the geometry of the first hydration layer on NaCl(100): the transition from a compacted (1×1) to a quasihexagonal $c(4\times2)$ configuration is caused by the *reduction* of the water coverage due to LEED induced desorption. The detailed explanation and discussion of these results are presented in Sec. III, following the computational details in Sec. II.

II. COMPUTATIONAL METHOD

All calculations have been performed using the Vienna *ab initio* simulation package (VASP),[16] implementing the density functional theory (DFT) within the Perdew-Wang 1991 (PW91) version of the general gradient approximation (GGA).[17] Projector augmented wave[18] (PAW) potentials were used to describe the Na, Cl, O, and H atoms. The surface is represented using a supercell/slab geometry, with periodic boundary conditions along the three spatial directions. The in-plane lattice constant (5.68 Å) has been determined from bulk calculations using the same parameters as in the rest of computations (fineness of the *k*-point sampling, plane-wave cutoff, PAW, etc.). The vacuum gap along the normal to the surface was 10.6 Å. This has proven to be sufficient to prevent any significant interaction between periodic images of the slab. In all calculations, the water was adsorbed on only one face of the slab, after confirming identical results, in selected cases, using a symmetric configuration with molecules adsorbed on both sides of the slab.

The slab consists of four NaCl layers with a 2×2 lateral periodicity for the investigation of the dimer, at 0.5 ML, and the investigation of the saturated layer at 2 ML coverage. A $c(4\times2)$ lateral periodicity is used for the proposed adsorbed configurations at 1.5 ML. We have verified from previous calculations[19] that a four layer slab is enough to produce

consistent adsorption properties. The two bottom NaCl layers were fixed during geometry optimization, whereas the rest of the atoms in the system were allowed to relax until all force components were smaller than 0.03 eV/Å. For all calculations a plane-wave cutoff of 400 eV and a $2\times2\times1$ Monkhorst-Pack k-point sampling were used. Using a larger plane-wave cutoff energy of 500 eV cutoff and a finer $4\times4\times1$ k-point mesh the total energy of an adsorbed water molecule on a four layer slab only changes by ~5 meV.

The adsorption energy per water molecule, E_{ads}, is calculated from

$$E_{ads} = -(E_{H_2O/NaCl} - E_{NaCl} - nE^{isol}_{H_2O})/n, \quad (1)$$

where $E_{H_2O/NaCl}$ is the energy of the optimized system containing n adsorbed molecules, whereas E_{NaCl} and $E^{isol}_{H_2O}$ correspond, respectively, to the energy of the relaxed NaCl(100) surface and of the relaxed water monomer isolated in vacuum, calculated in the same conditions (k points, cutoff, and unit cell) as the full optimized system. E_{ads} calculated in this way is the result of both water-water hydrogen bonding and water-surface interaction. The hydrogen bonding contribution, $E_{H\_bonding}$, can be estimated from

$$E_{H\_bonding} = -(E_{w\_layer} - nE^{isol}_{H_2O})/n, \quad (2)$$

where E_{w_layer} is the energy of a freestanding water layer with the same geometry as that found in the adsorbed configuration. Similarly, the water-surface interaction per molecule, $E_{H_2O\text{-}surf}$, is given by

$$E_{H_2O\text{-}surf} = -(E_{ads} - E_{H\_bonding}). \quad (3)$$

Notice that we have defined adsorption and other interaction energies above in such a way that their values are positive whenever the interactions are attractive.

III. RESULTS AND DISCUSSION

A. Low coverage

In a previous work, we found the optimum geometry of a water monomer adsorbed on the ideal NaCl(100) surface.[19] The molecule sits at 2.24 Å above the surface with the oxygen atom almost on top of a Na^+ and the plane of the water molecule nearly parallel to the surface. The calculated adsorption energy of 329 meV was in good agreement with other theoretical results.[9,12,13] Experimentally the adsorption energy of a water molecule on the NaCl(100) surface is difficult to determine at low coverage, since the water molecules tend to bind to surface defects,[8,20] with adsorption energies ~40% higher than those obtained by DFT computations for adsorption on perfect surfaces. As the coverage increases, water diffuses along the surface to form small hydrogen bonded networks. We have recently studied this diffusion process,[19] and it is likely to occur by several reorientation and pivoting processes with relatively low activation barriers. The calculated barriers, with values from 70 to 140 meV, are in good agreement with the experimental observation of diffusion at 298 K (Ref. 21) and molecular simulations of water clustering at room temperature.[22,23]

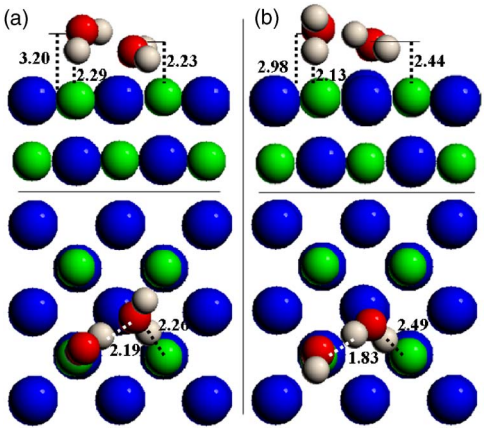

FIG. 1. Top and side views of two optimized water dimer geometries in a (2×2) NaCl(100) supercell. The distances and lengths are given in angstroms. The structure shown in panel (a) has an adsorption energy per water molecule E_{ads} of 396 meV, while for that in panel (b) E_{ads}=423 meV.

The formation of the dimer should be the first step in the cluster accretion. Here, we have studied two different structures for the water dimer adsorbed on NaCl(100), illustrated in Fig. 1. In these calculations we have represented the surface with a 2×2 supercell; thus, the water coverage corresponds to 0.5 ML. Although this is not a very low coverage, the interaction between neighboring dimers is almost negligible, and calculations employing a 4×4 supercell give adsorption energies differing by only 3%. Therefore, the relaxation of the dimer structure in a 2×2 supercell can be regarded as a good approximation for the description of an isolated adsorbed dimer. Dimer (a) follows the structure of the water dimer in the gas phase, determined by a wide range of electronic structure methods,[24,25] which has been also found adsorbed on other surfaces, such as graphite.[26] It is formed from a water molecule located 3.20 Å above the surface, with one hydrogen atom pointing to the Cl^- ion underneath ($H-Cl^-$ distance=2.29 Å) and the remaining hydrogen bonded to the adjacent water molecule (hydrogen bond of 2.19 Å). This second molecule lies 2.23 Å from the topmost NaCl layer, with its plane slightly tilted from the parallel with the closer H at 2.26 Å from the neighboring Cl^-, compared to 2.75 Å for the other $H-Cl^-$ "bond."

Dimer (b) in Fig. 1 is formed from dimer (a) by rotating both water molecules ~90° around an axis perpendicular to the surface that passes through their oxygen atoms. In this arrangement, the slightly tilted water molecule is located 2.44 Å above the surface, keeping one $H-Cl^-$ bond of 2.49 Å and one hydrogen bond to the adjacent molecule of 1.83 Å. The second molecule, situated 2.98 Å from the surface, has one hydrogen directed to the surface, with a $H-Cl^-$ bond of 2.13 Å. Geometrically, dimer (b) is comparable to that proposed by Park *et al.* on the basis of DFT (PBE GGA) calculations.[9] However, in our structure the down-pointing water molecule is adsorbed ~0.2 Å closer to the surface and, thus there is a slightly shorter water-water hydrogen bond.

The total energy of dimers (a) and (b) only differs by ~59 meV. The adsorption energy of the dimer (i.e., referred to the freestanding dimer in vacuum) is 533 meV for dimer (a) and 592 meV for the configuration (b). We can also cal-

culate the adsorption energy per water molecule forming the dimer (i.e., relative to the energy of two isolated water molecules); this varies from 396 meV for dimer (a) to 423 meV for dimer (b). In both structures the water molecules are hydrogen bonded to each other, conferring an additional stabilization to the adsorbed dimer compared to two separately adsorbed water molecules. From the difference between the total energy of the dimer system and twice the total energy of the adsorbed monomer, we can estimate a lower bound for the energy of the hydrogen bond of 134 and 188 meV for dimers (a) and (b), respectively. Clearly, the shorter hydrogen bond within the dimer favors configuration (b).

B. First hydration layer: "Bilayer" structures

When the coverage approaches the complete monolayer regime, water clusters and layered structures may coexist on the surface.[22] At 1 ML coverage we have optimized a (1×1) model similar to that proposed in previous works.[9,10,13,27] This structure consists of one water molecule per Na adsorption site, each molecule with an orientation similar to that of the isolated adsorbed monomer. This water monolayer sits 2.26 Å above the surface, and the adsorption energy per water molecule is 350 meV (see Table I). Therefore, the adsorption energy is only slightly higher than in the case of an isolated molecule. The low contribution of the hydrogen bonding, ~53 meV, was expected since water molecules are too far apart to have a significant interaction. Furthermore, the molecules adopt an orientation on the substrate similar to that of the adsorbed water monomer in order to maximize the water-surface interaction, which contributes ~297 meV to the adsorption energy. The fact that the adsorption energy per molecule for this (1×1) monolayer is substantially smaller than that found in the case of the "isolated" water dimers points to the important role of the hydrogen bond in determining the preferred structure of water clusters on NaCl(100). It seems clear that the most favorable structures should have a significant amount of water molecules connected through hydrogen bonds. However, the HAS experiments[7,8] give clear indications, at least under certain conditions, of a (1×1) pattern for the first hydration layer on NaCl(100) surface [although in some cases this pattern has been reported to transform to a $c(4\times2)$ periodicity after LEED irradiation[7]]. In summary, the results we have just presented indicate that it is quite unlikely that the observed (1×1) structure would correspond to an ordered monolayer of "disconnected" monomers as suggested by several authors.[9–11,13]

Indeed, the idea that the (1×1) structure should be assigned to 1 ML, understood as one water molecule per NaCl pair, is based on a preconception of the researchers and the computer convenience rather than in solid experimental evidence. Experimentally it is not straightforward to determine the exact water/NaCl ratio for the first adsorbed water layer. In fact, when the substrate remains unsaturated, the water molecules tend to diffuse along the surface to form more compressed structures, especially at ambient conditions.[19,22] Thus, it is reasonable to think that the observed (1×1) pattern could correspond to a structure of higher coverage than

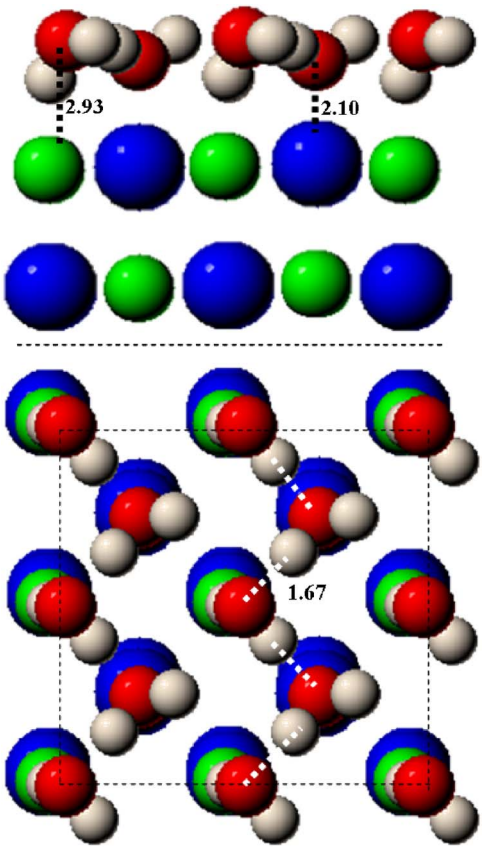

FIG. 2. Top and side views for an optimized (1×1) water bilayer at 2 ML coverage. The 2×2 NaCl(100) supercell, containing eight water molecules, used in the calculations is highlighted with black dashed lines. The adsorption energy per molecule is 571 meV. This structure was constructed from the dimer structures. The hydrogen bonds between the molecules are also schematically indicated with white dashed lines, and the numerical values are given in angstroms.

1 ML. Following this line of reasoning, we have found that a very stable (1×1) structure can be constructed at 2 ML water coverage instead of 1 ML. Hereafter this structure will be referred as the 1×1 bilayer. The optimized configuration is illustrated in Fig. 2. The 1×1-bilayer model is formed by zigzag chains of hydrogen bonded water molecules (the hydrogen bonds are schematically indicated by white dashed lines in Fig. 2). This compact (1×1) bilayer was constructed by combining the two water dimers studied previously at low coverage as building blocks. The quasiplanar and H-down water molecules are adsorbed with their oxygen atoms at 2.10 and 2.93 Å above the surface, respectively, and keeping a hydrogen bond of 1.67 Å, shorter than the 1.83 Å found in the isolated dimers. The adsorption energy of ~571 meV per water molecule (see 1×1 bilayer in Table I) has a hydrogen bond contribution of ~390 meV, whereas the water-surface interaction contributes only ~181 meV to the adsorption energy. Interestingly, this bilayer was constructed using the same 2×2 supercell used for our calculations of the isolated dimers. Thus the calculation was performed for a supercell containing eight water molecules. In spite of these additional degrees of freedom, and the relatively low symmetry of the structure, the arrangement of molecules preserved to a high degree of 1×1 periodicity supporting the plausibility of our proposal.

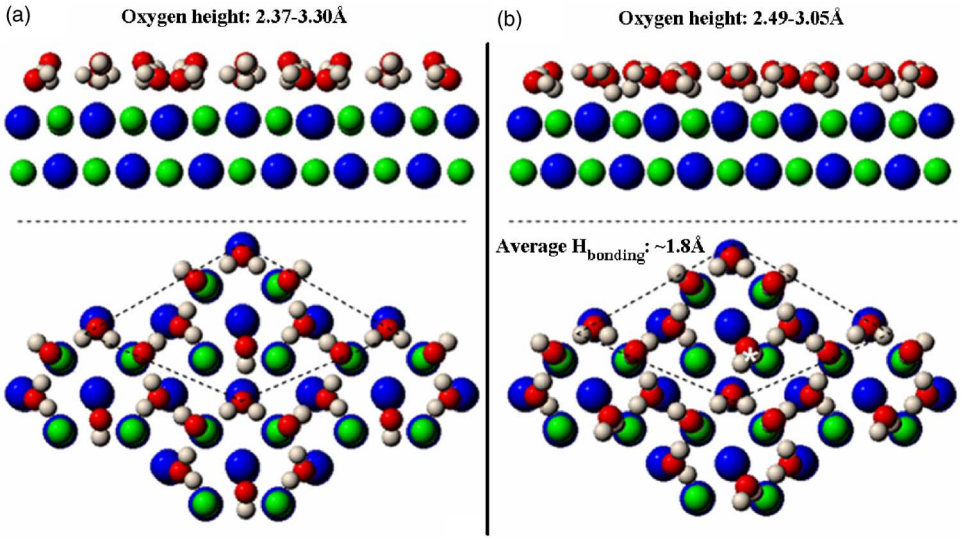

FIG. 3. Top and side views of the initial (a) and optimized (b) geometries of the $c(4\times2)$-bilayer *A* structure. The $c(4\times2)$ NaCl(100) supercell is highlighted with dashed lines. It contains six water molecules corresponding to 1.5 ML coverage. The adsorption energy per molecule is 572 meV. This structure was constructed from the dimer structures in Fig. 2. The only water molecule undergoing a strong rearrangement during the relaxation process is marked with a start in panel (b).

The binding energy per molecule is lower than that obtained with the same computational approach for a molecule in bulk ice;[28] however, it is greater than the binding energy of water molecules in small gas-phase clusters.[24] We believe that this indicates that although the water would prefer to optimize the hydrogen bonding to form bulk ice structures, at low coverages it will prefer to bind to the surface rather than form small clusters, i.e., in this case we expect wetting of the surface. It should be noted that E_{ads} for the 1×1 bilayer is similar to that computed for many putative water overlayer structures on transition metal surfaces. Although the experiments are clear on which surfaces wet, theoretical binding energies of overlayers still compare unfavorably in most cases with the binding of a molecule within bulk ice, even allowing for partial dissociation in very large unit cell structures on Pt(111) surfaces.[29] On Ru(0001), however, a chainlike structure of intact water molecules of alternating flat and hydrogen-down lines has been proposed,[30] and the more favorable match of substrate and ice lattice constants yields an E_{ads} only ~15 meV less favorable than the binding energy in bulk ice.

In the work of Toennies *et al.*, the observed transition from (1×1) to $c(4\times2)$ periodicities was attributed to a compression of the water layer, by the adsorption of ambient water molecules, together with a reorganization of the structure.[7] It is generally accepted that a LEED current may induce rearrangements of adsorbed water molecules, which in the case of water on NaCl(100) could be simple reorientations or small shifts of their adsorption sites, such as those presented in our previous work.[19] Another likely effect of electron irradiation is the desorption of adsorbates from the substrate. This has been largely studied in the case of metallic surfaces.[14,15] Chiba *et al.*[14] established the electron irradiation desorption threshold of ~2 eV for water adsorbed on iron oxide. Also, Sloan *et al.* observed water desorption from GaAs(100) induced by 50 eV electron irradiation at 100 K.[31] As the LEED experiments of Toennies *et al.*[7] were performed at electron energies ~90 eV, the partial desorption of the water layer could be a possible option. Since several authors have already proposed $c(4\times2)$ structures at a coverage of 1.5 ML, and taking into account our proposed 1×1 bilayer structure, it seems plausible that the transformation from the (1×1) to the $c(4\times2)$ periodicities is caused and accompanied by the change of water coverage from 2 to 1.5 ML.

Therefore, our next step has been to study $c(4\times2)$ geometries for 1.5 ML, corresponding to six water molecules per four NaCl units on the topmost layer. We propose two different $c(4\times2)$ adsorption geometries, in which the water molecules have been placed forming a hexagonal bilayer resembling a two dimensional icelike structure.

The first $c(4\times2)$ water layer configuration is based on a combination of both water dimer structures illustrated in Fig. 1. It consists of six water molecules, all threefold coordinated hydrogen bonded to their neighbors. They adsorb either parallel atop a Na^+, donating two hydrogen atoms to hydrogen bonds, or atop a Cl^- ion, with one hydrogen atom directed towards the surface, the other donated to a hydrogen bond [see Fig. 3(a)]. The initial oxygen heights above the surface, of 2.37 and 3.30 Å for the planar and down-pointing molecules, respectively, readjust during the optimization to 2.49 and 3.05 Å, resulting in a slight flattening of the water bilayer [Fig. 3(b)]. In the optimized configuration most water molecules maintain hydrogen bond lengths of ~1.8 Å, with the exception of the molecule marked with an asterisk inside the unit cell of Fig. 3(b). This molecule is attracted by its right-hand neighbor, weakening its left-hand hydrogen bond. Consequently, the orientation of the left-side molecule is dominated by bonding to the underlying Cl^- ion, with a H–Cl distance of ~2.68 Å. The overall structure of the adsorbed layer thus consists largely of threefold coordinated molecules with only one broken hydrogen bond per unit cell. This quasihexagonal ice bilayer structure is similar to that obtained by Park *et al.*, using the same computational methods (although PBE GGA functional was used rather than PW91 GGA).[9] However, the structure proposed by Park *et al.* appears to have two broken hydrogen bonds instead of one. This could explain the 20% increase in adsorption energy (to ~572 meV) found for our model.

In our quasihexagonal $c(4\times2)$ configuration the hydrogen bonding contribution dominates the adsorption energy

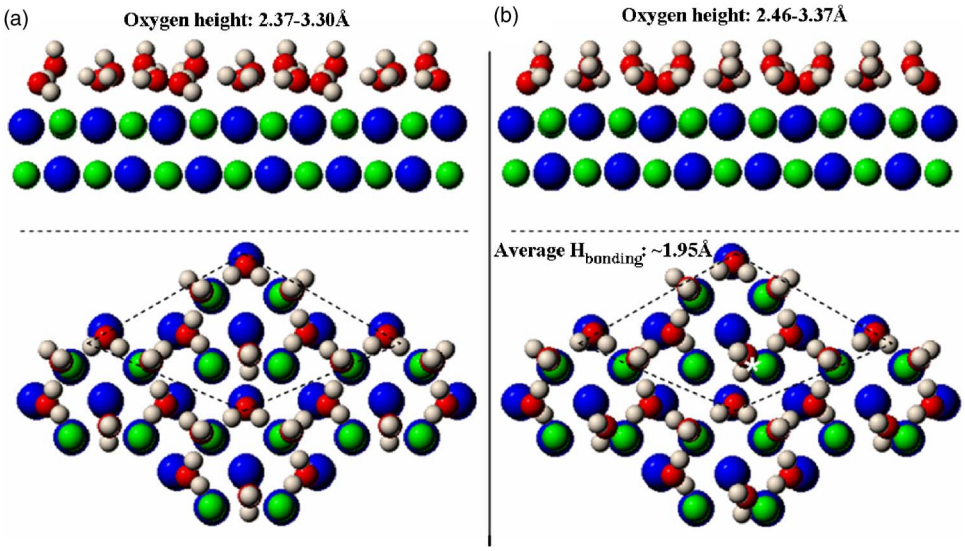

FIG. 4. As Fig. 3 but for the $c(4\times2)$-bilayer *B* structure. The adsorption energy per molecule is now reduced to 522 meV. This bilayer structure is formed by alternating planar and H-up water molecules.

by more than 67% [we refer to this structure as $c(4\times2)$-bilayer *A* in Table I]. Energetically, both the (1×1) and $c(4\times2)$ structures are comparable, clearly indicating a competition between the shorter and stronger hydrogen bonds in the twofold coordinated water molecules on the 1×1 structure and the longer hydrogen bonds between threefold coordinated water molecules in the $c(4\times2)$ structure.

We have proposed a second structure following the $c(4\times2)$ symmetry, constructed by reorienting the downwards-pointing water molecules from the previous $c(4\times2)$ initial configuration. The dangling hydrogen atoms are now pointing away from the surface [see Fig. 4(a)]. This configuration diminishes the attractive interaction with the surface allowing greater freedom for the water bilayer to adopt its preferred hexagonal structure, keeping all hydrogen bonds. However, during relaxation the oxygen atoms sited on top of the Cl^- ions suffer a strong repulsion from the surface and the hydrogen-up molecules readjust to lie ~3.37 Å from the surface, whereas the planar molecules remain at ~2.46 Å above the surface. Therefore, the corrugation of the bilayer increases and the length of the hydrogen bond becomes on average ~1.95 Å. Furthermore, as in the previous case, due to the incommensuration of the ice and NaCl unit cells, the molecule marked with an asterisk in Fig. 4(b) is attracted more by its right-side neighbor, resulting in a hydrogen bond of ~1.8 Å. In consequence, the left hydrogen bond weakens and the bonding of the left-side molecule to the underlying Cl^- ion becomes more significant, giving a $H-Cl^-$ bond of ~2.2 Å. The adsorption energy of this configuration is also dominated by the hydrogen bonding [see $c(4\times2)$-bilayer *B* in Table I]. However, the adsorption energy per water molecule, 522 meV, is ~50 meV lower than in the previous configurations. This is attributed to the generally weaker water attachment to the surface.

IV. CONCLUSIONS

We have performed DFT calculations using GGA-PW91 approximation to investigate the structural and bonding properties of the first hydration layer adsorbed on the NaCl(100) surface. We have paid particular attention to the role of hydrogen bonding and, as a particular case, the use of water dimers as the basic building blocks for the construction of a complete water layer.

For water dimers at low coverage, we found that the hydrogen bonding between the molecules confers an extra stabilization of at least 134–188 meV compared to isolated adsorbed monomers and, as a consequence, the adsorption energies are considerably higher for the dimer than for the isolated molecule and even for typical models of a monolayer with (1×1) periodicity and a coverage of water per surface Na^+ ion.

We have proved that very favorable bilayer geometries can be constructed using the dimers as building blocks. In particular, we have compared a new structure with (1×1) periodicity at 2 ML coverage based on zigzag chains of hydrogen bonded molecules, with two quasihexagonal bilayers with a $c(4\times2)$ periodicity at 1.5 ML coverage. All these structures have adsorption energies per water molecule above 500 meV. Computed binding energies show that one of our quasihexagonal structures is more stable than previous proposals based on DFT calculations for the $c(4\times2)$ phase.[9,13] This might be due to the smaller number of broken hydrogen bonds in the icelike structure of our bilayer.

The hydrogen bond between molecules plays a fundamental role in the structures proposed in the present work. As a result, they have much higher adsorption energies than the monolayer models constructed to maximize the water-surface interaction that have been proposed by several authors to explain the (1×1) periodicity observed in the experiments,[9,10,12,13] and which can be visualized as a collection of water monomers with very weak intermolecular interactions. The (1×1) bilayer at 2 ML and one of our $c(4\times2)$ structures, the so-called $c(4\times2)$-bilayer *A*, have very similar high adsorption energies per water molecule of ~570 meV. This is due to the balance between the shorter (and presumably stronger) hydrogen bonds in the case of the (1×1) structure and the larger coordination (number of hydrogen bonds) in the case of the $c(4\times2)$ quasihexagonal configurations. In a very recent paper, which appeared during the completion of this work, Yang *et al.*[32] have studied sev-

eral structures with different water coverages on NaCl(100) using a methodology similar to that used here. Our data agree with some of their high coverage results. These findings open a new scenario to explain the experimental uncertainty in the determination of the structure of the first hydration layer. It becomes plausible that the transition from the (1×1) to the $c(4\times2)$ periodicities, observed upon electron irradiation, would take place through the partial desorption of the original (1×1) 2 ML bilayer and the rearrangement of the remaining water molecules to form a quasihexagonal structure with $c(4\times2)$ periodicity. This gives a new interpretation of the results of Toennies *et al.*[7]

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